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CITATION:

Hakamada, Masataka ...[et al]. Electrochemical actuation of nanoporous Ni in NaOH solution. Materials Letters 2012, 70: 132-134

ISSUE DATE:

2012-03-01

URL:

http://hdl.handle.net/2433/237628

Electrochemical actuation of nanoporous Ni in NaOH solution

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Abstract: The fabrication of a bilayer-stacked Ni electrochemical actuator is reported. The stacked bilayer sheet composed of bulk and nanoporous Ni deformed when a potential of ±1 V was applied in aqueous NaOH solution, which is the first report of nanoporous Ni exhibiting actuation characteristics. Actuation is considered to have a strong relationship with the electrical double layer, because cyclic voltammetric measurements suggested that the effect of oxygen adsorption on the surface was minor. The results suggest that nanoporous Ni can be used as an actuator, and it has potential in being applied for commercial use because of its low price and high availability.

Keywords: Nanoparticles / Interfaces / Nanocomposites / Sensors / Surfaces / Thin films

1. Introduction

The direct conversion of electrical energy to mechanical energy is important in many applications including robotics, artificial muscles, optical displays, prosthetic devices, optical communication and micromechanical devices [1–3]. Thus, increasing effort to improve the actuation characteristics is being made. Piezoelectric ceramics [4], shape memory alloys [5] and magnetostrictive materials [6] are well-known conventional actuation materials and their applications have been commercialized. However, these conventional materials have drawbacks including an upper limit of operation temperature, voltage requirements of up to 100 V [7] and small work densities per cycle. Polymer actuators have been

proposed as an alternative because of their low weight and cost, flexibility and wide range of material options. However, the Faradaic process involved in the actuation requires dopant diffusion and structural changes [7], which limit the response, life cycle and energy conversion efficiency [7].

Aggregated Pt nanoparticles in an electrolyte have recently been investigated as a novel and promising actuator [8], as their high output and good mechanical strength are ideal for miniaturization. Various nanoporous metals including Au [9] and Au-Pt [10] fabricated by dealloying can be also used as actuators in an electrolyte. In the current study, we show that nanoporous Ni also possesses actuation characteristics in aqueous NaOH solution. Ni is cheaper and more abundant than Au and Pt, so nanoporous Ni may be a more preferable actuator material than nanoporous Au and Pt.

2. Materials and Methods

Commercially available Ni (>99.9%) and Mn (>99.9%) ingots were melted together by arc melting under an Ar atmosphere to produce a precursor $Ni_{0.3}Mn_{0.7}$ alloy ingot. The $Ni_{0.3}Mn_{0.7}$ ingot was then annealed for homogenization at 1173 K for 24 h under an Ar atmosphere, followed by water-quenching to avoid the formation of Ni-Mn intermetallic species. The $Ni_{0.3}Mn_{0.7}$ ingot was then cold-rolled by several passes to a thickness of 0.2 mm [11].

Fig. 1 illustrates the fabrication of the actuator sheet composed of a bulk and nanoporous Ni stacked bilayer. Ni was initially electrodeposited onto the rolled Ni-Mn sheet. The electrolyte was composed of $NiSO_4 \cdot 6H_2O$ (150 g/L) and $NiCl_2 \cdot 6H_2O$ (15 g/L), and the pH was adjusted to 4.0 using H_3BO_3. The working electrode and counter electrode were the Ni-Mn film and bulk Ni sheet, respectively. A direct current density of 30 mA/cm^2 was applied for 1 h at 333 K. The Ni-electrodeposited Ni-Mn sheet was then heated at 773 K for 2 hrs under Ar flow, to allow diffusion bonding to occur. The (Ni-Mn)/Ni sheet was then dealloyed in 1 mol/L $(NH_4)_2SO_4$ at room temperature. A three-electrode electrochemical cell controlled by a potentiostat was used for dealloying. The counter electrode, working electrode and

reference electrode were platinum wire, (Ni-Mn)/Ni sheet and a saturated calomel electrode (SCE), respectively. An electrochemical potential of −650 mV (vs SCE) was applied on the working electrode for 30 h until very little current was detected. The dealloying conditions were similar to those reported previously [11].

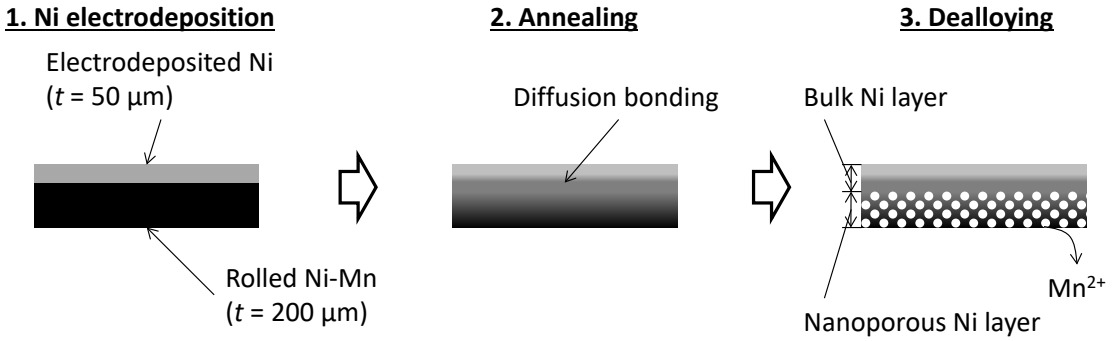

Figure 1.

Microstructures of the nanoporous/bulk Ni bilayer sheet were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDXS). Cyclic voltammetry (CV) was conducted using a potentiostat and a typical three-electrode electrochemical cell, with a Pt plate counter electrode, SCE reference electrode and sample working electrode in aqueous 1 mol/L NaOH solution.

To determine the actuation in nanoporous Ni, the nanoporous/bulk Ni bilayer sheet (length, width and thickness of 40, 3 and 0.25 mm, respectively) was immersed in 1 mol/L NaOH as a working electrode. The counter electrode was a platinum wire. The potential difference between the electrodes was switched from −1 to +1 V every 10 seconds, and the movement of the specimen was observed with a stereomicroscope. A strain gauge was pasted on the bulk Ni side of the specimen so that the strain was simultaneously monitored during switching of the applied potential. A characteristic evaluation of the actuator with the strain gauge was carried out previously [12].

3. Results and Discussion

Dealloying resulted in a composite foil consisting of a 200-μm-thick layer of nanoporous Ni covered

with 50 μm of solid Ni. A typical SEM image of the nanoporous Ni is shown in Fig. 2a. Image analyses showed that the ligament diameter was approximately 10 nm. The EDXS spectrum in Fig. 2b showed that Mn dissolved selectively from $Ni_{0.3}Mn_{0.7}$.

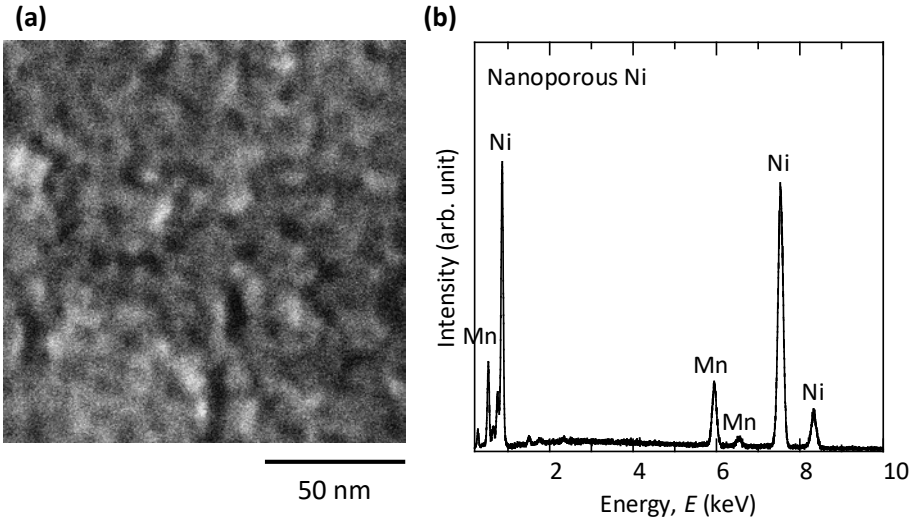

Figure 2.

When the potential difference between the electrodes was switched from −1 to +1 V in the NaOH solution, the specimen moved reversibly in response to the changes in potential. The tip of the sheet moved by up to 0.5 mm.

The variation in strain during potential switching is shown in Fig. 3, where the positive strain means the expansion of nanoporous layer. The strain was well-aligned with the voltage change; i.e. the strain increased when +1 V was applied and vice versa. A fast strain response was obtained, similar to the case reported for nanoporous Au [9].

The adsorption and desorption of oxygen have been reported to have an effect on the actuation [10] and mechanical response [13] of nanoporous Au. CV curves in Fig. 4 show no clear peaks for the adsorption and desorption of oxygen, suggesting that oxygen sorption has a minor effect on the actuation of nanoporous Ni, although direct comparison between actuation (Fig. 3) and CV (Fig. 4) is difficult because of the difference in the electrode setup (2-electrode and 3-electrode).

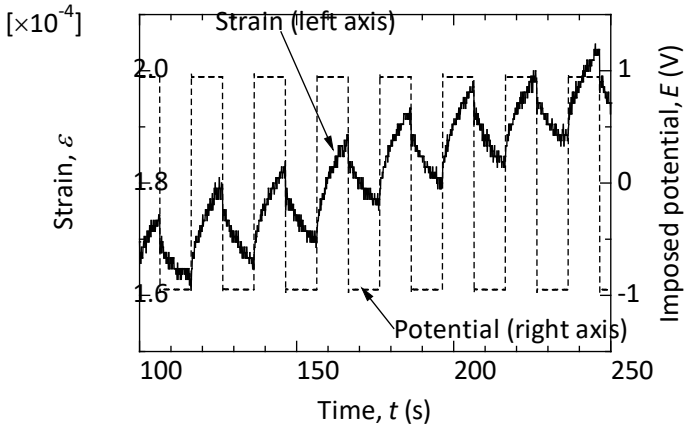

Figure 3.

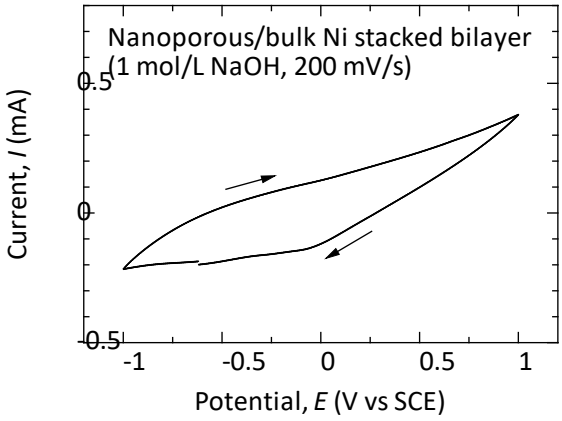

Figure 4.

The dependence of surface stress on the surface charge density for a clean metal surface has been known as electrocapillarity [14], and theoretically predicted based on the jellium model [15,16]. Therefore, nanoporous metals exhibit actuator characteristics because they have a large surface-to-volume ratio and considerable charge induced on their surface [8,9]. It has been clarified that modified bonding in the space-charge layer within the metal surface has an important effect on the change in surface stress [8,9,16,17]. That is, induced charge varies the net charge in space-charge layers at the metal surface. Thus, the change in the electronic density of states leads to a change in surface stress. If this concept is valid, then each metallic species should exhibit different actuation behavior.

The coexistence of lattice expansion and contraction at the surface of nanoporous metals [18] may vary the electronic density of states of the surface. Therefore, we also consider that nanoporous metals exhibit

actuator characteristics not only because they have a large surface area, but also because the electric density of states is changed by the disordered lattice at the surface [17]. An investigation of the difference between nanoporous Ni and Au in actuation characteristics based on electronic theory may be helpful for further understanding of this concept.

In the case of nanoporous Au and Pt, clean metallic surface state shows expansion under the positive potential sweeping [10], which was also observed in the present nanoporous Ni. On the other hand, according to Pourbaix diagram of Ni species [19], contribution of hydrogen adsorption/desorption due to possible naturally-oxidized surface state of Ni should be taken into consideration. 3-electrode setup of electrochemical cell during actuation test will be useful for further clarification [10].

4. Conclusions

The actuation of nanoporous Ni in NaOH has been demonstrated for the first time, in which the strain varied sensitively with the change of induced potential. CV results suggested that oxygen sorption had a minor effect on the actuation of nanoporous Ni in NaOH aqueous solution. In contrast to Au and Pt, Ni has magnetic properties [20] and the present nanoporous Ni actuator may possess synergistic effects of piezoelectric and magnetostrictivity.

Acknowledgments

The authors thank Prof. T. Yao and Prof. T. Yabutsuka (Kyoto Univ.) for assistance with SEM observations.

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Figure Captions

Figure 1. Preparation of the nanoporous/bulk Ni stacked bilayer sheet.

Figure 2. (a) SEM image and (b) EDXS spectrum of nanoporous Ni fabricated by dealloying. EDXS indicated 18 at.% of residual Mn.

Figure 3. Strain variation during potential switching of the nanoporous/bulk Ni actuator in aqueous NaOH.

Figure 4. Cyclic voltammetry curves for the nanoporous/bulk Ni stacked bilayer in 1 mol/L NaOH.